

## SYNERGISTIC EFFECT ON SOLVENT SWELLING OF COAL

Tetsuo Aida, Eisaku Suzuki, issei yamanishi, and Masaki Sakai  
Department of Industrial Chemistry, Faculty of Engineering at Kyushu  
Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka 820, JAPAN

Keywords: coal, solvent swelling, synergistic effect

### INTRODUCTION

It has long been curious question why the coal swelling exhibited a synergistic effect in a certain binary solvent system. In 1986, Hombach[1] observed a significant synergistic effect on the solvent swelling of coal in the mixed solvent such as amine and methanol, and tried to rationalize with a hypothesis which the change of the solubility parameter of the mixed solvent was responsible for that phenomena.

In the meantime, Iino et al.[2] also found a quite interesting binary solvent system on the coal extraction, that is, the mixture of CS<sub>2</sub> and N-methyl pyrrolidinone(NMP) gave a maximum extraction yield at their 50:50(vol-%) mixing conditions. This solvent system is well-known as a "*Magic*" solvent for the coal extraction, of which detailed mechanism has not yet been clarified.

In the course of our studies on the coal swelling, we have learned that the coal has an significant steric requirement[3] toward the penetrating solvent molecules due to the cross-linking macromolecular network structure. Also, the maximum swelling ratio of coal swelling was very much depending on the donorability of the swelling solvent, as previously pointed out by Marzec[4], probably because of the specific interaction between the solvent molecule and the cross-linking network structure formed by the relatively weak bonding interactions, such as hydrogen bonding, charge transfer bonding,  $\pi$ - $\pi$  bonding and even the van der Waals bonding interactions. These findings are now extending to our new sight of the coal chemistry, the elucidation of synergistic effects on coal swelling and the empirical determination of a "Coal Affinity Parameter".[5] Eventually, we could categorize the synergistic effects on the solvent swelling into the three types of the mixed solvent systems.

In this paper, we present our recent experimental results concerning the mechanism of synergistic effect appeared on the solvent swelling of coal, especially focusing on Type-I and Type-II.

### EXPERIMENTAL

The chemical reagents were commercial products (Gold label grade) which were used without further purification. Solvents used in this study were dried over appropriate drying agents and distilled before use. Coals from the Ames Coal Library and Argonne National Laboratory were ground, seized in N<sub>2</sub> atmosphere, dried at 110°C under vacuum overnight, and stored under a dry nitrogen atmosphere.

The measurement of the solvent swelling of coal was carried out by means of our hand-made instrument, and the experimental procedures were same as previously reported.[6]

### RESULTS AND DISCUSSION

#### 1. Synergistic effects on coal swelling in mixed solvent

As reported by Hombach, a coal swelling in a mixture of methanol and tertiary amine, such as dimethylaniline, trimethylamine, or trimethylamine affords a significant synergistic effect on its equilibrium swelling values(Q).

Figure 1 shows the typical example obtained our swelling measurements which is exhibiting the relationship between Q-value and the swelling rates (V-value) vs. concentration of methanol on the Illinois No.6 coal swelling in triethylamine/methanol mixed solvent.

It is quite interesting that in spite of the large synergistic effect on the Q-value there was almost no effect on the V-value (swelling rates). This fact strongly suggests that the synergistic phenomena appearing on this solvent system will not very much depend on the specific molecular interaction between tri-methylamine and methanol. We like to categorize this type of swelling system, as "Type-I".

Meanwhile, it has long been well-known phenomenon in the coal chemistry that the benzene-methanol mixed solvent enhanced its coal extractability. Actually, as far as our swelling measurements, both individual solvent can not give us a large amount of Q-

value, but the mixed solvent system has demonstrated completely different figures on their swelling parameters ( $Q$  &  $V$ ) as shown in Figure 2. In this case, not only the  $Q$ -value, but also the  $V$ -value exhibited large synergistic effects on the solvent composition.

Obviously, there are several interesting features on this swelling behavior, suggesting the different swelling mechanism from the Type-I synergistic effect described above. Namely, in this case, both the  $Q$ -value and the  $V$ -value showed large synergistic effects on the solvent compositions. This means that some specific interactions will exist between each solvent molecule toward the macromolecular network structure of coal. We can categorize this type of swelling, as "Type-II".

Almost ten years ago, Iino et al.[2] reported so-called "magic solvent system" on a coal extraction. Since then, any detailed information concerning the extraction mechanism did not come out in the literatures. We have initiated a study on the rationalization of the mechanism of the *Magic solvent extraction* by means of the solvent swelling technique.

In Figure 3, a solvent swelling phenomena of Illinois No.6 coal in CS<sub>2</sub>-NMP system measured by our instrument was demonstrated.

As expectedly, the significant synergistic effect was observed on both the  $Q$ -value and the  $V$ -value like a Type-II swelling system described above. As far as the swelling data shown in Figure 2, and 3, it seems to be quite difficult to rationalize the difference on the swelling mechanism between them. However, there are quite interesting data suggesting different type of a specific molecular interaction between both solvents like a kind of an electron donor-acceptor complex formation, of which detailed discussions will appear in our next paper.

Anyway, we like to categorize this type of synergistic effect as "Type-III".

## 2. "Type-I" synergistic effects on coal swelling

Some years ago, we had revealed the steric requirement of coal towards penetrating solvent molecules.[3] Coal exhibits a significant steric restriction to the penetrating molecules probably because of their cross-linking network structure like a "molecular sieve". For example, the initial swelling rates of Illinois No.6 coal in  $n$ -, sec-, iso- and tert-butylamine were  $3.7 \times 10^{-1}$ ,  $6.8 \times 10^{-2}$ ,  $3.1 \times 10^{-2}$ , and  $6.2 \times 10^{-3}(\text{min}^{-1})$ , respectively. This means that the swelling rate ( $V$ -value) of Illinois No.6 coal in a sterically bulky  $t$ -butyl amine was 60 times slower than that of a less sterically hindered  $n$ -butylamine.[3] Therefore it is quite difficult to evaluate the accurate equilibrium swelling value ( $Q$ ) in the bulky molecule solvent system, because of the very slow swelling rate, i.e., in the case of  $t$ -butyl amine its swelling was still continuing even after 10 days.

Meanwhile, as shown in Figure 4, we have found that this steric requirement of coal could be dramatically relieved in a mixed solvent system such as a methanol solution. Namely, in this solvent system, the equilibrium swelling value ( $Q$ ) of the sterically hindered molecule seems to be increased by the addition of a small amount of methanol, and the further increase of the methanol concentration results the exactly same  $Q$ -values of the less hindered molecule.

In order to confirm this speculation, we had conducted a dynamic swelling measurements of Illinois No.6 coal in the 20%-MeOH / Et<sub>3</sub>N solution. The result is demonstrated in the Figure 5 comparing with the one in CS<sub>2</sub>/NMP mixed solvent.

In the case of MeOH/Et<sub>3</sub>N solvent system, a strange behavior was observed at the initial stage of the coal swelling. Namely, a rapid penetration of solvent molecules into the coal matrix was induced within a minute after the mixing of coal and solvent, and then a slow but steady swelling was followed it.

It will be quite interesting to examine the solvent composition change at the initial stage of such coal swelling as shown above, because we can assume what kind of solvent molecule predominantly penetrated into the coal matrix. For this experiment we had carefully arranged the experimental condition as follows: The ratio of the coal and solvent was determined by a calculation from their ratio at the equilibrium swelling, which will make us easy to determine a small change of the solvent compositions in the supernatant by means of gas-chromatography. The initial contact between coal and solvent was performed by the introduction of the mixed solvent into the previously evacuated test tube in which the coal sample was placed. The results obtained are shown in Figure 6.

Very interestingly, the MeOH-concentration in the mixed solvent significantly decreased at early stage of swelling, which seemed to be comparable to the change of swelling volume of coal.

All of these experimental data strongly suggest that the coal swelling in the binary

solvent system composed by a sterically hindered molecule and a less hindered molecule will result an initial coal/solvent-gel formation induced by the predominant penetration of the less hindered solvent molecule. Actually, in according with our previous swelling measurement in the neat solvent system, Illinois No.6 coal swelled in methanol 60times faster than in t-butyl amine.[3] Thus in the binary solvent swelling system a methanol molecule has to predominantly penetrate into the coal, inducing a significant relaxation of a steric requirement due to the cross-linking network structure of coal, which will make the sterically hindered molecule like a triethylamine easy to penetrate into the coal matrix. We would like to call this type of steric relaxation as "Wedge Effect" of the mixed solvent demonstrating in Figure 7.

Actually, the solvent swelling was always involved with a sterically hindered molecules as a counter part of methanol, like a trimethylamine or dimethyl aniline.

In order to verify our speculation discussed above, we took another advantage to use a cross-linked synthetic polymer (styrene-divinylbenzene co-polymer: Bio-bead SX, BIO-Rad Ltd.), which had the known covalent cross-linking density and chemical structures.

Figure 8 shows our experimental data, which was obtained by using a hexamethyl phosphoramide (HMPA) as a sterically hindered component and a dimethylformamide (DMF) as a less bulky component. Obviously, there is a dramatic increase of the Q-value of HMPA by the addition of small amount of DMF.

All of these experimental data discussed above seems to be consistent with that the Type-I synergistic effect will be induced by the relaxation of the steric requirement of coal resulted by the initial formation of the coal-gel due to the predominant penetration of the less hindered solvent molecule.

### 3. "Type-II" synergistic effects on coal swelling

Just recently, we had developed a reliable chemical determination of the oxygen functionality in coal,[7] and learned that there were significant amount of carboxylic acid functionality, phenolic hydroxyl and alcoholic functionality in even bituminous coal like Illinois No.6 coal. Based on our preliminary analysis of coals by means of this new technique, the content of these acidic hydroxyl functionality in Illinois No.6 coal (pyridine-extract) reached up to 1.5, 12, and 10 units over 100 carbon atoms, respectively.[8] This means that the density of the functionality in the macromolecular network structure of coal is approximately one unit per 16 carbon skeleton. This is just an amazing fact, because the most of these oxygen functionality in coal are potentially capable to form a hydrogen bonding which is thought to play a major role for inducing the apparent cross-linking, as illustrating in Figure 9.

This modeling is our standpoint to understand the mechanism of the "Type-II" synergistic effect on coal swelling.

There may be at least two key factors for distinguishing Type-II from Type-I synergistic effects. Namely, the Type-II can be observed even in the mixed solvent composed of less hindered molecules, and also exhibits a significant synergistic effect on the swelling rate (V-value in Figure 2).

If the coal had such polar hydroxyl functionality as mentioned above, a benzene molecule must have a big trouble in its initial stage of the penetration, because of the blocking by the polar cross-linking like a hydrogen bonding, even if there were some comfortable spaces inside of the macromolecular network structure. In this case, very naturally, the coexistence of a polar and small sized molecules like a methanol in the solvent will induce a destruction of an apparent cross-linking structure constructed by a hydrogen bonding with same manor as Type I synergistic effect discussed above.

It will be also true that the polar solvent like a methanol could be in trouble to penetrate into the macromolecular network structure, because of the apparent cross-linking due to  $\pi$ - $\pi$  interactions between aromatic rings. In this case, the coexistence of benzene in the solvent must help its penetration by breaking such non-polar bonding interactions in macromolecular network structures.

This speculation, "Co-operative Swelling" can be verified by the same treatments as applied to the Type-I synergistic effect shown in Figure 6. The solvent compositions during the coal swelling in a benzene/MeOH mixed solvent were analyzed by using the same technique as described in Type-I synergistic effect. The results obtained are summarized in Figure 10.

It is obvious that there is an interesting difference between the Type-I and Type-II synergistic effects on the solvent composition change during a coal swelling, that is, in the case of the Type-II synergistic effect, both solvent systems, 20vol%-benzene/MeOH and 20vol%-MeOH/benzene, exhibited the predominant penetration of benzene and MeOH

molecule into the macromolecular net work structure of coal, respectively. These phenomena can result in a synergistic effect because of their cooperative destruction toward apparent cross-linking structure formed by polar and non-polar bonding interactions in the coal matrix.

Actually, we often experience a curious solvent dependency of the solubility of the condensed aromatic compounds, for example, benzene can dissolve anthracene very nicely, but a methanol, even DMF can not dissolve it. This phenomenon is suggesting that the aromatic-aromatic interaction in coal may be far larger than our imagination.

Anyway, in this solvent system, the major role of the methanol molecule is thought to be the relaxation of the apparent cross-linking structure caused by destruction of the hydrogen bonding. If so, the combination with a molecule which has more stronger hydrogen bonding ability than methanol, like trifluoroacetic acid ( $pK_a=2.5$ ) must induce a more larger synergistic effect. The same idea will be applicable to the swelling experiment, in which a strong base like a tetra-butylammonium hydroxide ( $n\text{-Bu}_4\text{NOH}$ ) is used as a destruction agent of a hydrogen-bonding cross-linking in the macromolecular network structure of coal.

These facts can be rationalized with the decreasing cross-linking due to hydrogen bonding in the macromolecular network structure of coal. Under these circumstances the equilibrium swelling value ( $Q$ ) and the swelling rate ( $V$ -value) of the coal swelling must be increased by their cooperative destruction of the apparent cross-linking structure of coal.

## CONCLUSION

The synergistic effect observed on the coal swelling in binary solvent were categorized three types, Type-I, Type-II, and Type-III. The Type-I can be rationalized by the relaxation of the steric requirement of coal induced by the initial formation of coal-gel. The Type-II synergistic effect consistent with the cooperative destruction of the apparent cross-linking structure, such as hydrogen bonding or a  $\pi$ - $\pi$  bonding interaction.

## ACKNOWLEDGEMENT

A part of this research was supported by the grant from The Japanese Ministry of Education through The 148th Committee on Coal Utilization in The Japan Society of Promotion of Science (JSPS).

## REFERENCES

- (1) Hombach, H.P., *Fuel* **59**, 465(1980)
- (2) Iino, M., Matsuda, M., *Fuel*, **62**, 744(1983)
- (3) Aida, T., Fuku, K., Fujii, M., Yoshihara, M., Maeshima, T., *Energy & Fuels*, **5**, 79(1991)
- (4) Szeliga, J., Marzec, A., *Fuel*, **62**, 1229(1983)
- (5) Aida, T., Yamanishi, I., *Prepr. Sekitan Kagaku Kaigi*(Japanese), 169(1998)
- (6) Aida, T., Squires, T.G., *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*, **30**, 95(1985)
- (7) Aida, T., Yoshinaga, T., Yamanishi, I., Tsutsumi, Y., *Proceedings of 9th International Conf. on Coal Science, Essen*(Germany), 179(1997); Aida, T., Hiram, N., Tsutsumi, Y., *Prepr., Pap.-Am. Chem. Soc., Div. Fuel Chem*, **42**, 218(1997); Yoneda, M., Yamanishi, I., Aida, T., *Prepr., Sekitan Kagaku Kaigi*(Japanese), 97(1998)
- (8) Aida, T., unpublished results

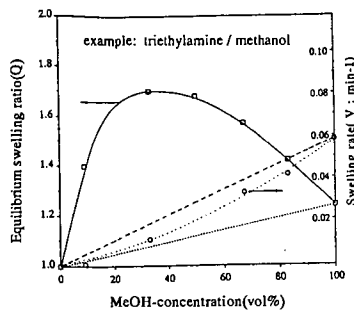


Figure 1. Swelling of Illinois No.6 in binary solvent (Et3N/MeOH)

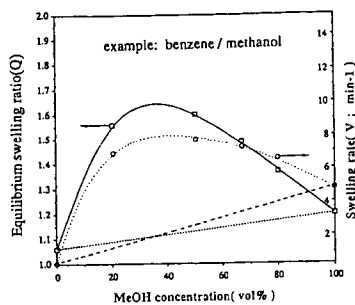


Figure 2. Swelling of Illinois No.6 in binary solvent (benzene/MeOH)

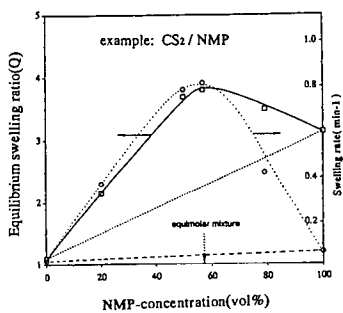


Figure 3. Swelling of Illinois No.6 in binary solvent (CS2/NMP)

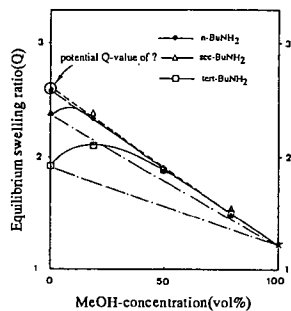


Figure 4. Swelling of Illinois No.6 in binary solvent (BuNH2/MeOH)

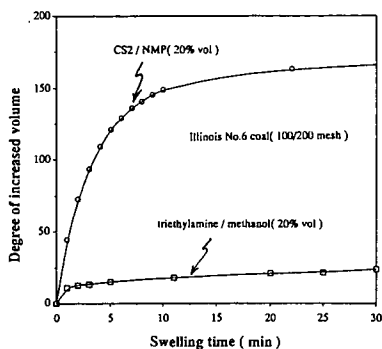


Figure 5. Swelling behavior of Illinois No.6 in binary solvent

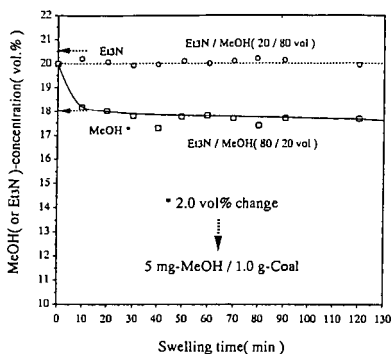


Figure 6. Composition change in binary solvent during coal swelling

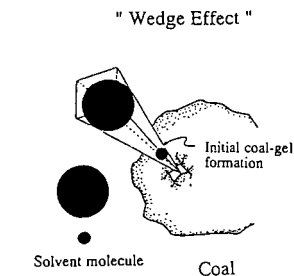


Figure 7. Penetration model of mixed solvent into macromolecular network structure of coal

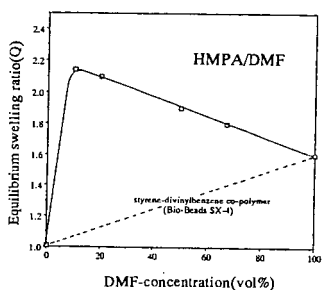


Figure 8. Solvent swelling of cross-linked synthetic polymer in HMPA/DMF mixed solvent

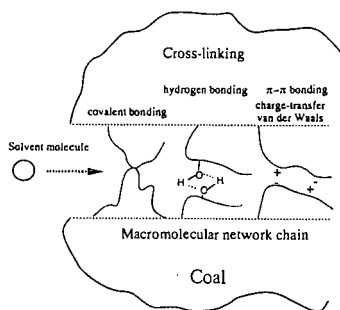


Figure 9. Penetration model of solvent molecule into macromolecular network structure of coal

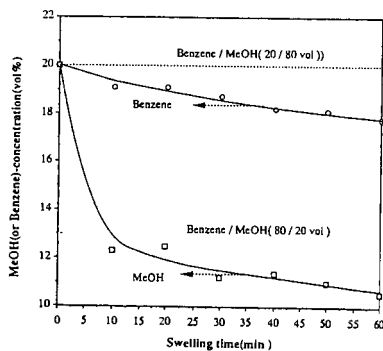


Figure 10. Composition change in binary solvent during coal swelling